

# High Index Materials for 193 nm and 157 nm Immersion Lithography

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Support to NIST from Office of Microelectronics Programs at NIST  
and International SEMATECH

# Outline

- Why high index materials for immersion lithography?
  - Needed to gain benefit of high index fluids
  - Reduce lens size

- High index materials

## I. Alkaline Earth Fluorides

- Intrinsic birefringence issue
- Mixed solid solutions

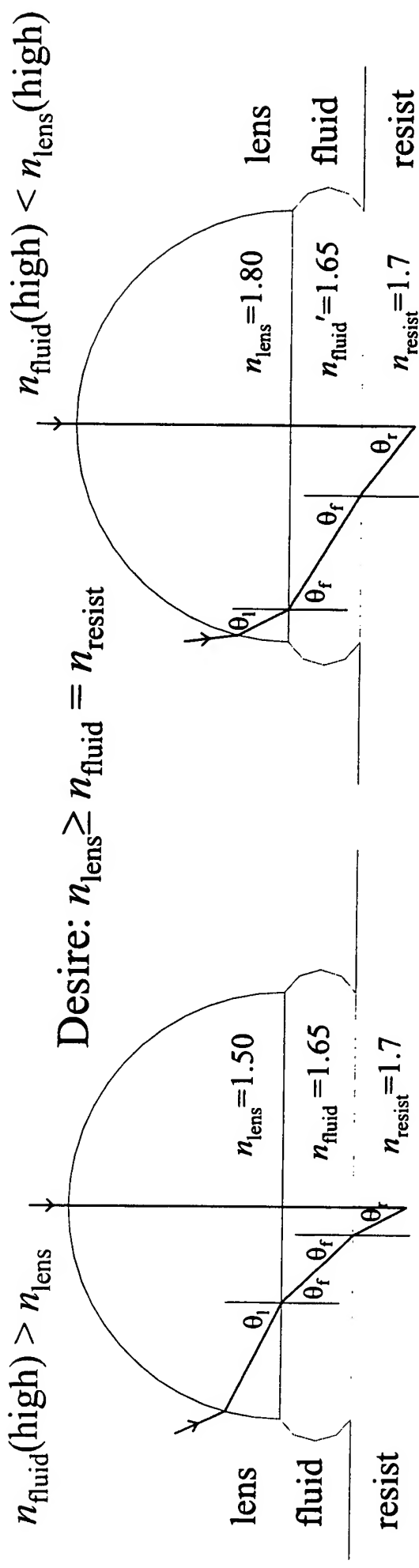
## II. Alkaline Earth Oxides

# High Index Materials

Point of immersion fluid is to enable higher angles into resist  $\Rightarrow$  incr. NA.  
Requires higher angles into the fluid from lens.

$\Rightarrow$  increasing size of lens to contain aberrations

If  $n_{\text{fluid}} > n_{\text{lens}}$ , ray bends towards normal in fluid  $\Rightarrow$  loose max. NA



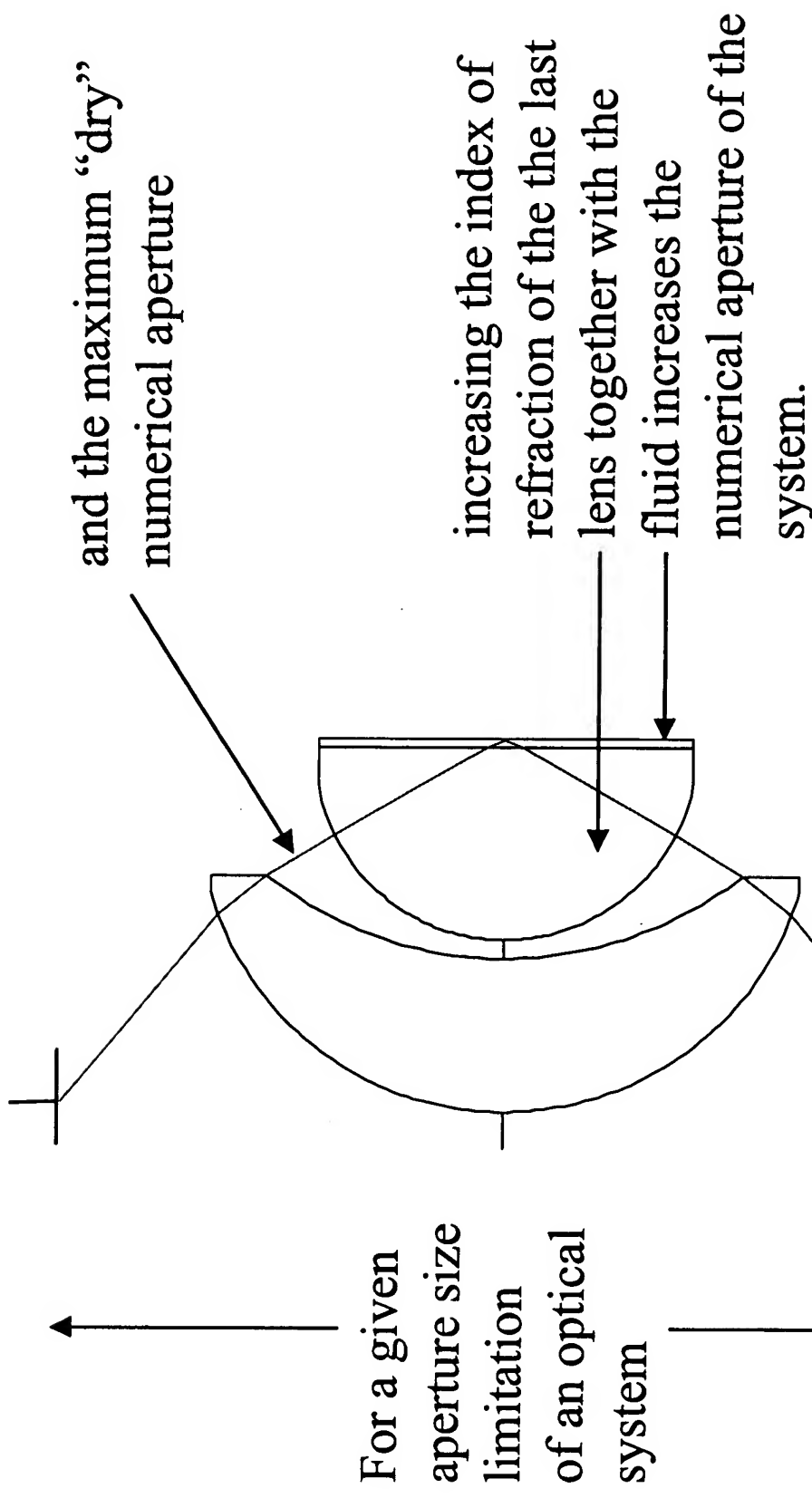
To gain full benefit of high  $n$  fluids need last element(s) with high  $n$ .  
( $n_{\text{lens}} > n_{\text{CaF}_2}(193\text{nm}) = 1.50$ )

Program to find and characterize candidate high index, isotropic (193nm transparent) materials:

Only need for last small lens element(s)  $\Rightarrow$  lower specs, easier to achieve

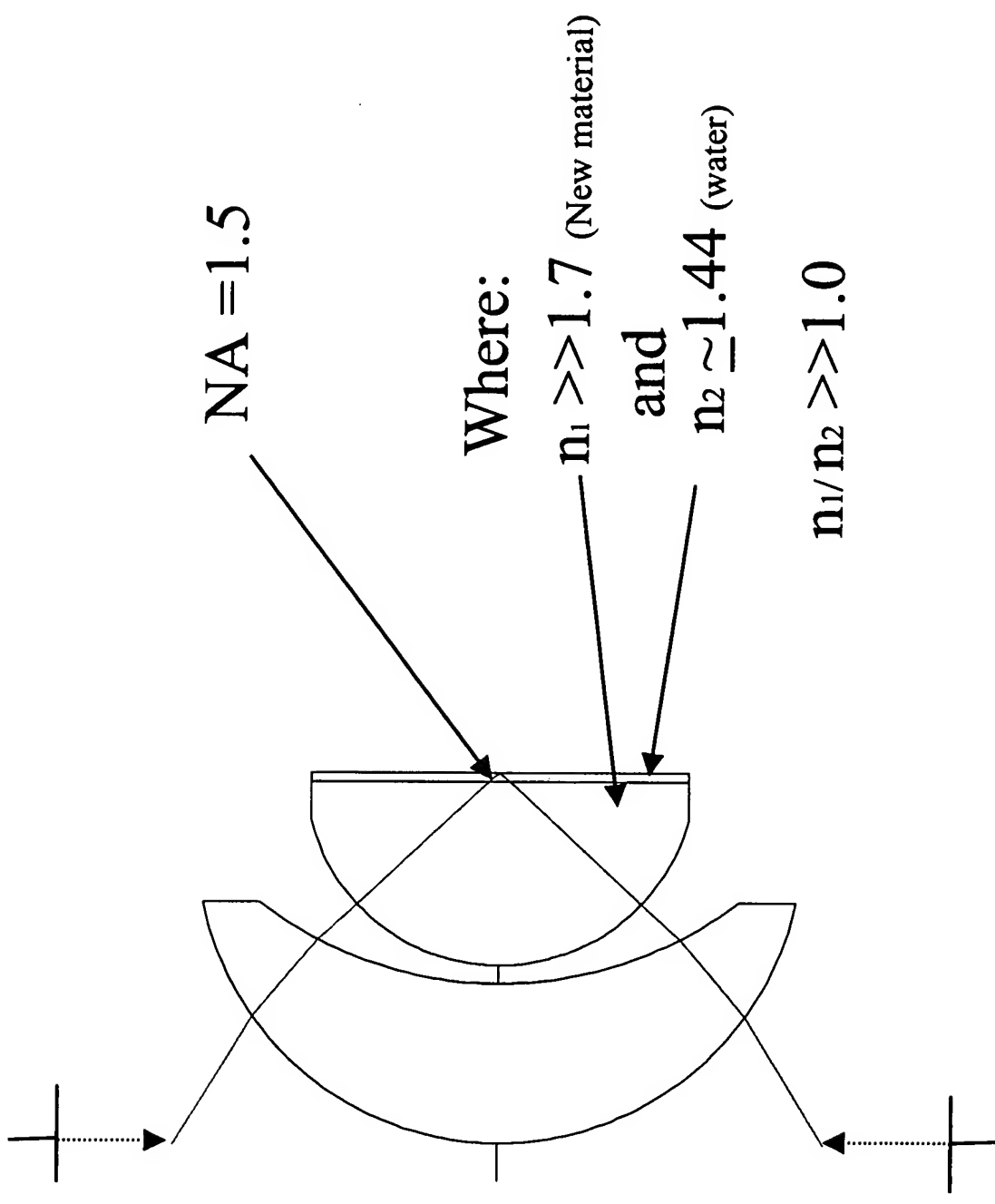
# Increase System NA With Given Aperture Limit

To improve resolution with immersion fluid  $\Rightarrow$  larger angles  $\Rightarrow$  bigger optics



# Reduce Maximum Aperture With Given NA

If fluids indices are limited but even higher index materials where  $n_1/n_2 \gg 1.0$  can be found, then the maximum aperture is reduced



# Reduce Polarization Effects

Ideal case:  
If the fluid index and the material index are the same as the resist, index then refraction is minimized and polarization effects are reduced.

Assuming:  
 $n_3 = 1.7$  (resist)

NA  $\sim 1.5$

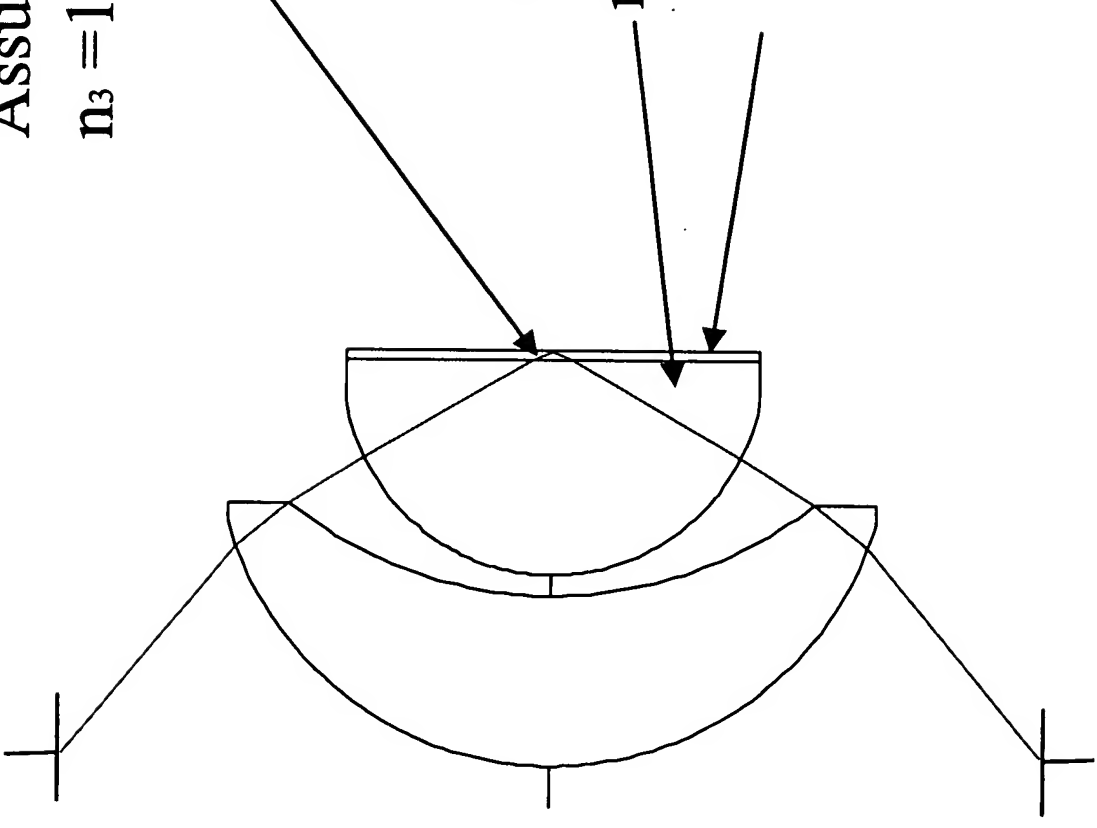
Where:

$n_1 = 1.7$  (New material)

and

$n_2 = 1.7$  (New Fluid)

$n_1/n_2 = 1.0$



# High Index Materials Program

- Program to find and characterize candidate high-index UV optical materials:
  - For 193nm and 157nm
- Since would only need for last small lens element(s)  $\Rightarrow$  specs. easier to achieve (lens small)  
lower specs. (small fraction of total lenses)
- Material requirements:
  - transparent at 193 nm (157 nm)
  - grown as large, high-quality single crystals
  - isotropic optical properties  $\Rightarrow$  cubic symmetry
  - good extrinsic properties: index homogeneity, stress-induced birefringence, laser durability, ...
- Must be able to contain effects of intrinsic birefringence.

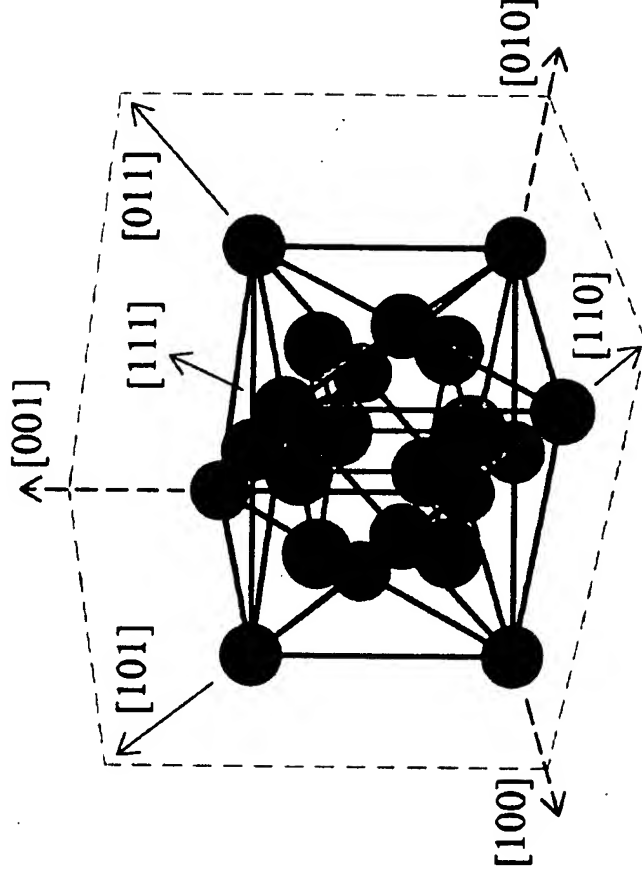
# Alkaline Earth Fluorides

Group II Fluorides:  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$

- All band gap energies  $> 8 \text{ eV}$   
 $\Rightarrow$  all transmit at 193nm and 157 nm
- All cubic crystals:  $\text{Fm}\bar{3}m$   
 (Ca on FCC lattice, F on SC Lattice)

Periodic Table (Partial) showing elements relevant to the study:

Group	1	2	13	14	15	16	17	18
Period 1	H	He						
Period 2	Li	Be	B	C	N	O	F	Ne
Period 3	Na	Mg	Al	Si	P	S	Cl	Ar
Period 4	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Period 5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru
Period 6	Cs	Ba	La	Hf	Ta	W	Re	Os
Period 7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs



increasing  
band gap  
energies

Material	Abs Edge	Index (193nm) (20°C)	Index 157nm (20°C)
$\text{CaF}_2$	123 nm	1.50	1.56
$\text{SrF}_2$	128 nm	1.51	1.58
$\text{BaF}_2$	134 nm	1.58	1.66



# High $n$ UV Optical Materials – BaF<sub>2</sub>

Property	193 nm (20 °C)	157 nm (20 °C)
index	1.58	1.66
$dn/d\lambda$ (nm <sup>-1</sup> )	-0.002	-0.0044
$dn/dT$ (°C)	$1 \times 10^{-6}$	$8.6 \times 10^{-6}$
$q_{11}$ (10 <sup>-12</sup> Pa <sup>-1</sup> )	-1.7	-2.4
$q_{12}$ (10 <sup>-12</sup> Pa <sup>-1</sup> )	2.0	2.0
$q_{11} - q_{12}$	-3.7	-4.4
$q_{44}$ (10 <sup>-12</sup> Pa <sup>-1</sup> )	1..1	1.30
IBR (nm/cm)	19	33

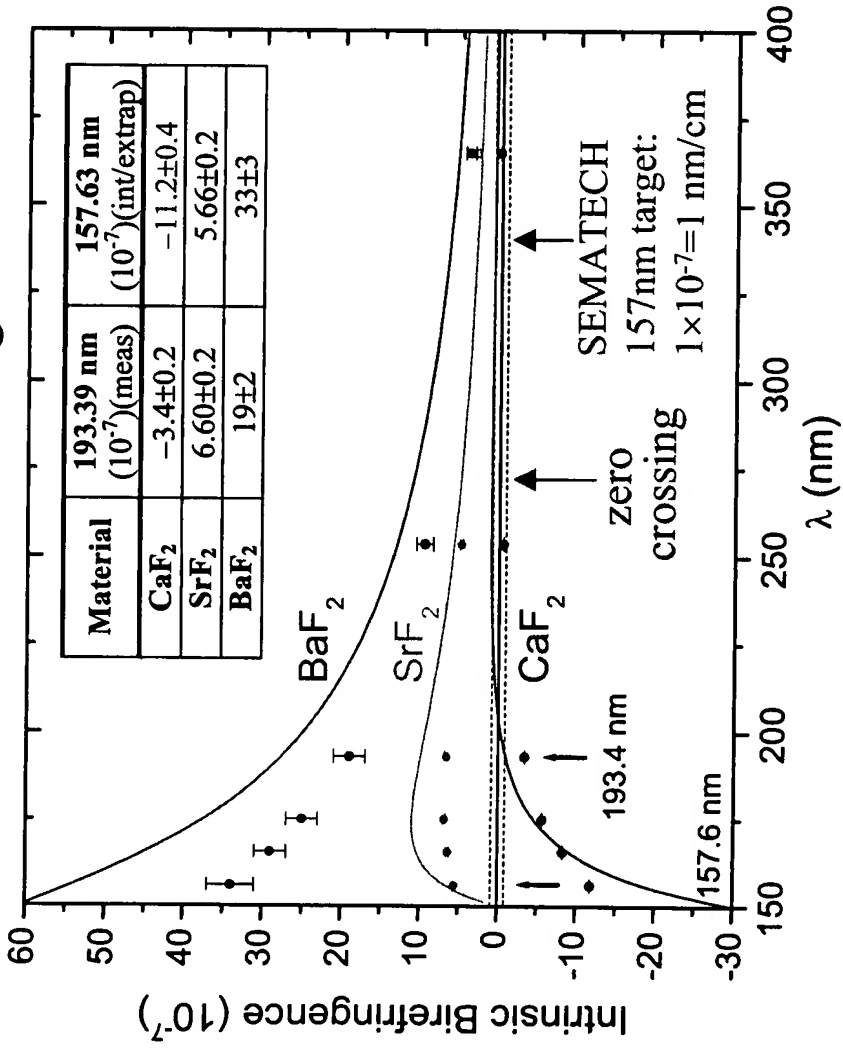
John Burnett, “Stress Birefringence, Intrinsic Birefringence, and Index Properties of 157 nm Refractive Materials”, SEMATECH Final Report (LITJ216) (2002).

- NIST previously characterized opt. prop. – color corrector 157 nm.
- Extensive experience, BaF<sub>2</sub> brought to material specs. nearly good enough for large 157nm litho lenses (with minimal effort).
- Durable to 193 nm and 157 nm excimer radiation.
- Miscible: Ba<sub>x</sub>Sr<sub>1-x</sub>F<sub>2</sub> (all  $x$ ) and Ba<sub>x</sub>Ca<sub>1-x</sub>F<sub>2</sub> near  $x = 0,1$ .
- Can possibly increase index (above 1.58 at 193 nm) by mixing.
- High intrinsic birefringence: 19 nm/cm (193nm), 33 nm/cm (157nm).

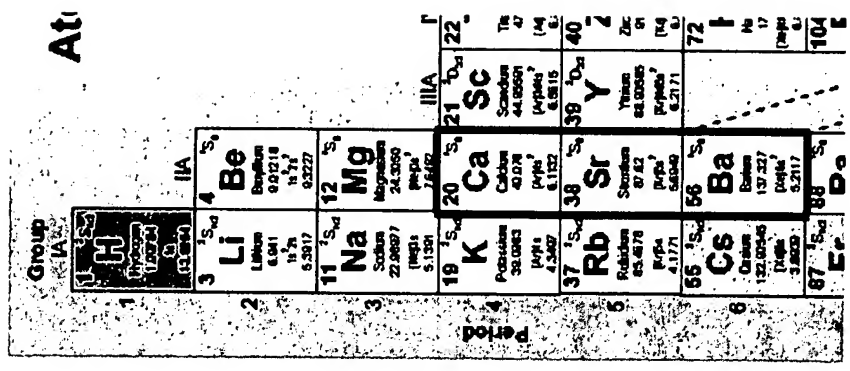
# Eliminating Intrinsic Birefringence With Mixed Crystals

- Demonstrated  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  have intrinsic birefringence and anisotropy.
- Effect governed by single parameter.

Intrinsic Birefringence

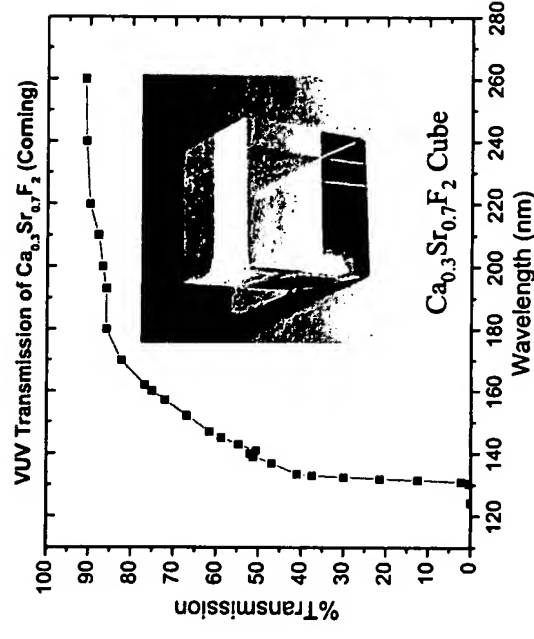


- $\text{SrF}_2$  and  $\text{BaF}_2$  have IBR of opposite sign compared to  $\text{CaF}_2$ .
- $\text{Ca/Sr}$ , and  $\text{Ba/Sr}$  miscible for all  $x$ ,  $\text{Ca/Ba}$  miscible for some  $x$ .  
 $\Rightarrow$  value of  $x$  for  $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$  or  $\text{Ca}_x\text{Ba}_{1-x}\text{F}_2$  can be chose so that  $\Delta n = 0$ .
- Calc.  $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{F}_2$  nulls IBR at 157.6 nm;  $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{F}_2$  nulls IBR at 193.4 nm.



# $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ Crystals

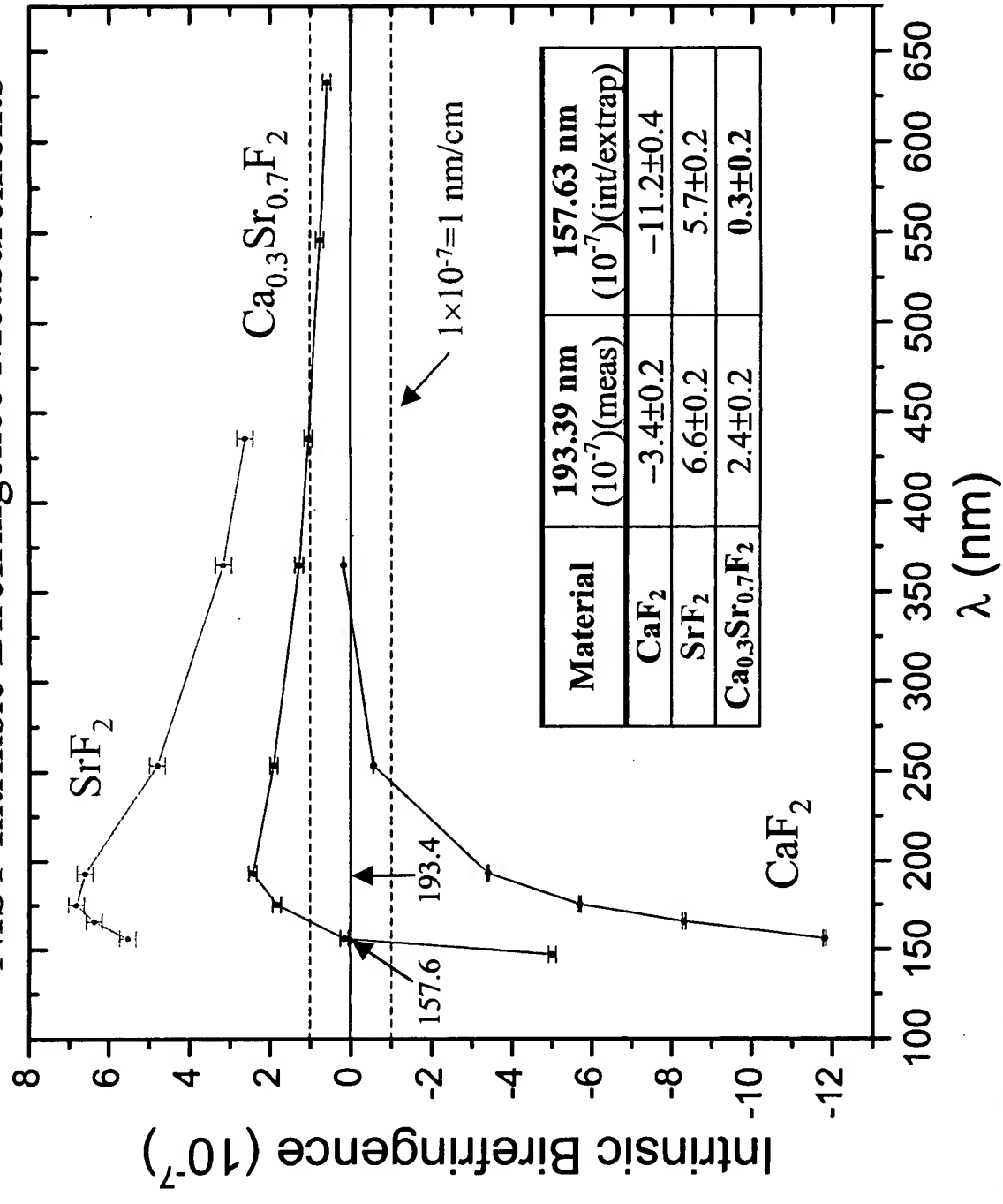
- $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$  mixed crystals for  $x=0.1-0.9$  grown by Corning, North Brookfield.
- Vacuum Stockbarger technique – no attempt to optimize process for  $x$ .<sup>1</sup>
- Key results:
  - Single crystal ingots free of gross imperfections.
  - All have high transmission at 157nm (varies monotonically with  $x$ ).
  - Laser durability and induced  $\alpha$  good.
  - Stress-induced birefringence relatively high  $\sim 5$  nm/cm.
- Post growth anneal (2003).
- Oriented and prepared 25mm cube nominally  $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{F}_2$ , with stress-induced birefringence  $\sim 0.6$  nm/cm.



<sup>1</sup>C. M. Smith and R. W. Sparrow, “Optical Properties of  $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$  Crystals”, 157 nm Symposium, Antwerp (2002).

# Eliminating Intrinsic Birefringence In $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$

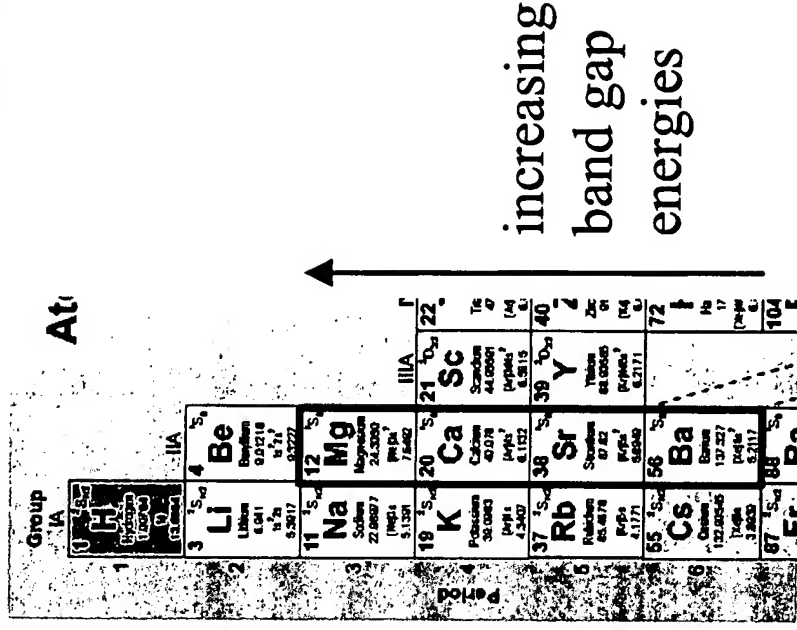
## NIST Intrinsic Birefringence Measurements



- $\text{Ca}_{0.3}\text{Sr}_{0.7}\text{F}_2$  eliminates intrinsic birefringence nearly completely at 157nm!
  - Expect that  $\text{Ca}_{0.7}\text{Sr}_{0.3}\text{F}_2$  will eliminate intrinsic birefringence at 193nm.
- Note:  $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$  does not increase  $n$  substantially. But,
- 1) useful because incr. specs. 2) proof of principle for higher  $n$  materials

# Alkaline Earth Oxides

Group II oxides: MgO, CaO, SrO, BaO  
(Related oxides: e.g.,  $\text{MgAl}_2\text{O}_4$  - spinel)

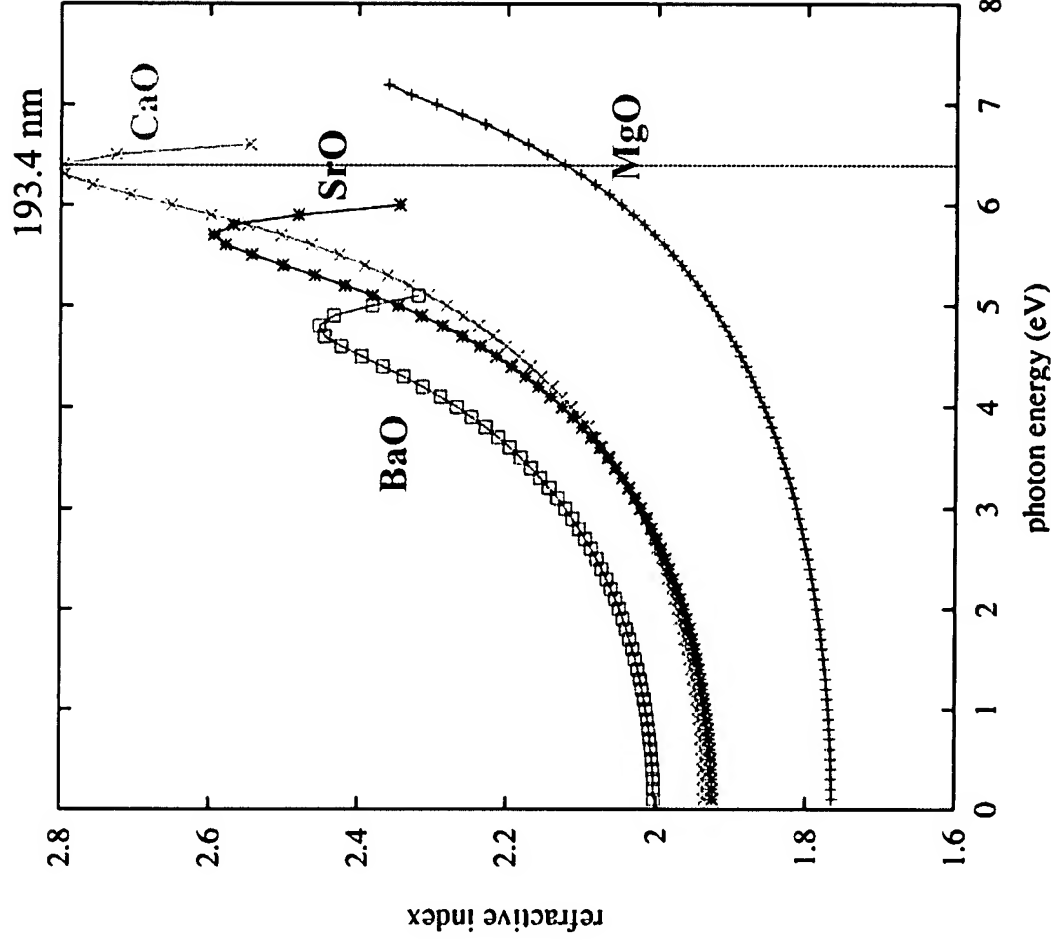


- MgO and  $\text{MgAl}_2\text{O}_4$  high transmittance at 193nm.
- All cubic crystals: rocksalt structure.  
(spinel – FCC)
- MgO and CaO miscible ~10%.
- MgO best known
  - high  $T_c$  superconductor substrate.
- Insoluble in water.
- High physical strength and stability.
- Cleaves (111) and (100) directions.
- High melting point 2852 °C.

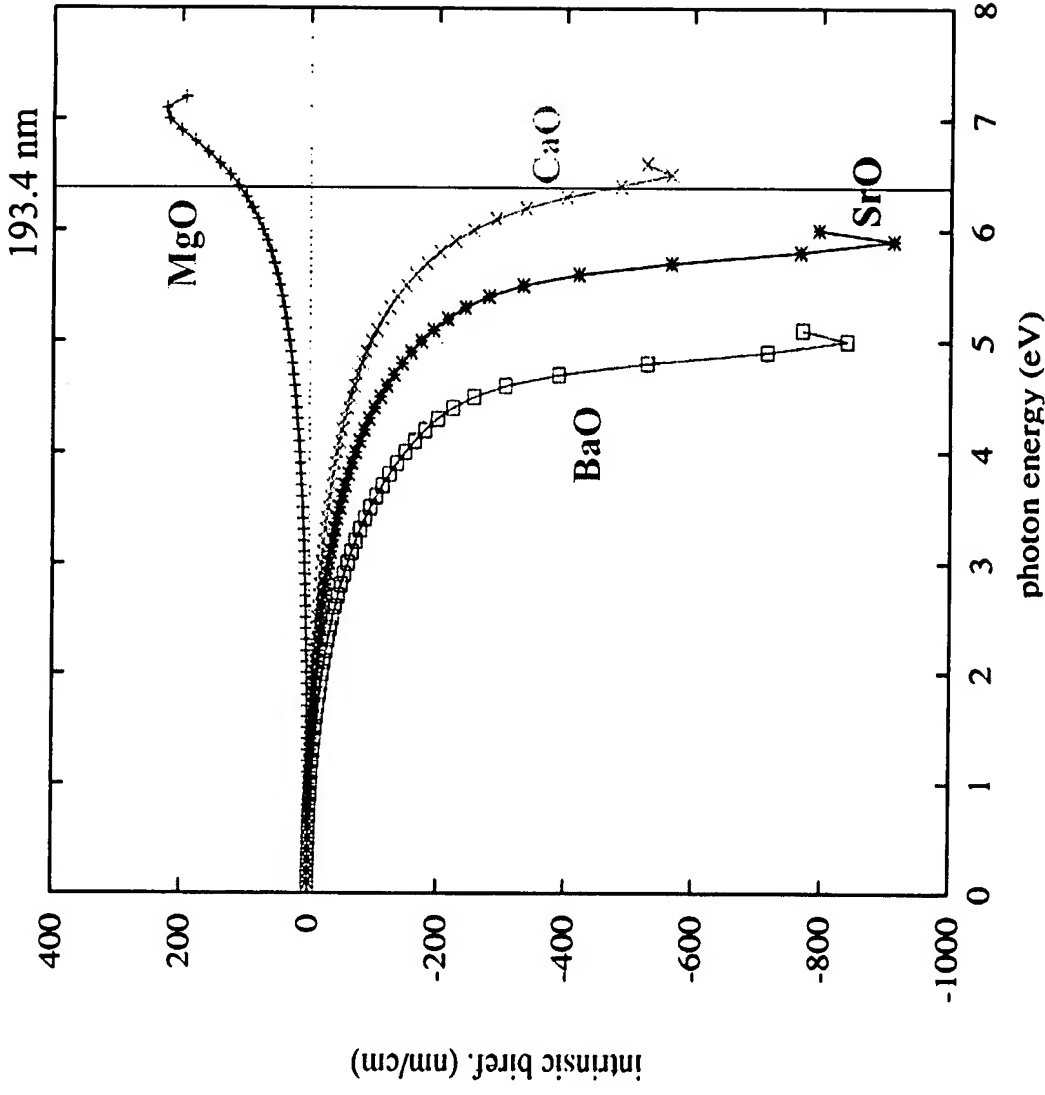
Material	Abs Edge	Index (193nm) (20 °C)
MgO	165 nm	2.0
CaO	> 200 nm	2.7
SrO	> 200 nm	
BaO	> 200 nm	
$\text{MgAl}_2\text{O}_4$	160 nm	1.8

# Alkaline Earth Oxides – Calculated Dispersions

- First principles calculations (preliminary): Eric Shirley, NIST (7/13/04).
- CaO mixes with MgO to increase index above 2.0.

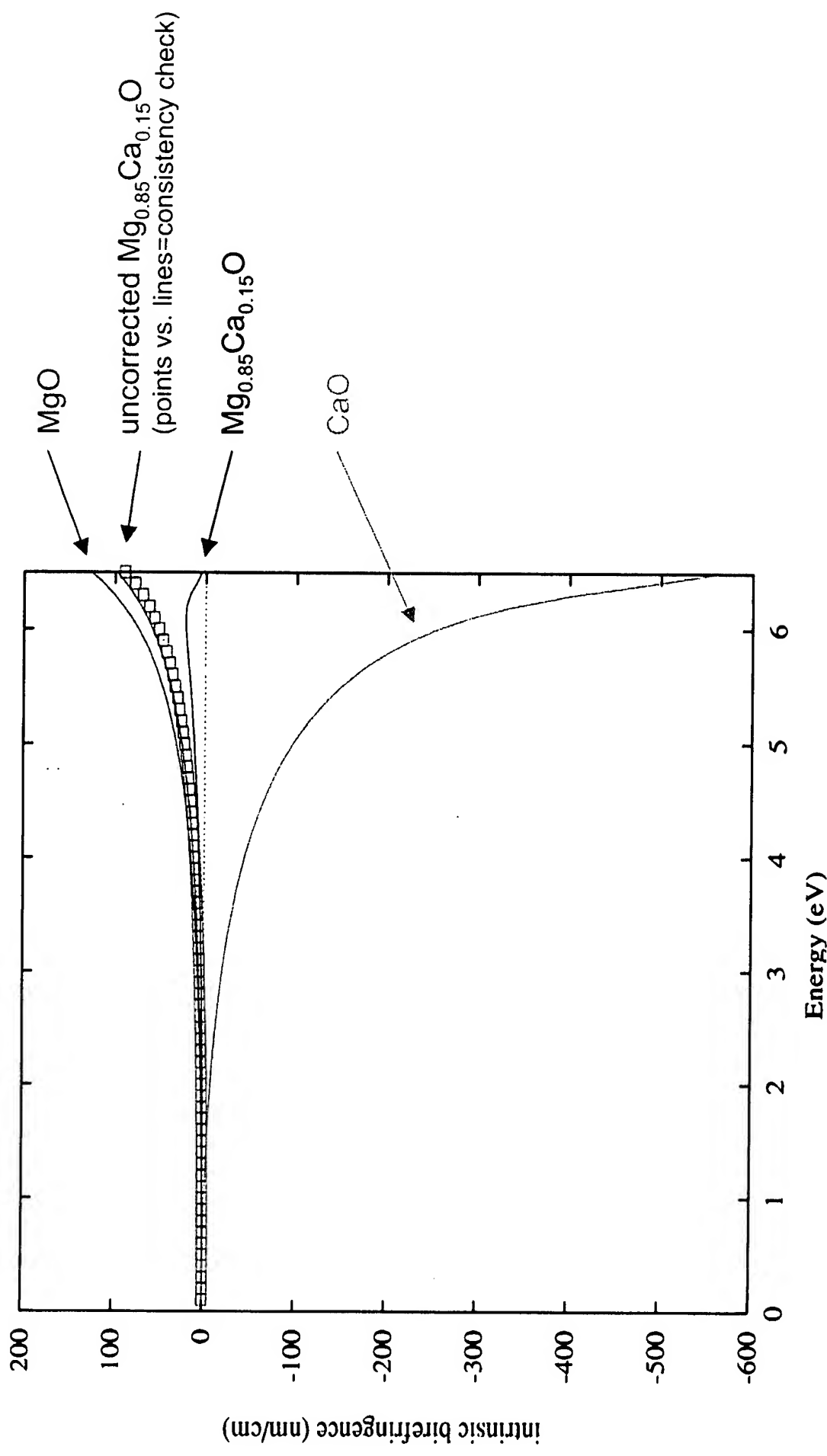


# Alkaline Earth Oxides – Calculated IBR



- MgO has intrinsic birefringence opposite in sign to that of others.
- As with  $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ , expect can mix in small amount of CaO into MgO to get  $\text{Mg}_x\text{Ca}_{1-x}\text{O}$  with no intrinsic birefringence!

# Simulation of IBR in MgO/CaO Mixture



- Calculations of intrinsic birefringence in  $\text{Mg}_{0.85}\text{Ca}_{0.15}\text{O}$  (preliminary).
  - Indicates no intrinsic birefringence at 193.4 nm.



# Conclusions

- High index materials needed for last optical element of 193 nm (157) immersion systems to gain full benefits of high index fluids.
  - enables higher NA for given aperture if you increase indices of fluid and lens material together.
  - enables smaller lens designs for a given NA.
- Some gain using  $\text{BaF}_2$  as last element material.
- Demonstrated that mixed crystals can eliminate intrinsic birefringence in Group II fluorides ( $\text{Ca}_x\text{Sr}_{1-x}\text{F}_2$ ). Proof of principle for general case.
- More dramatic gains with  $\text{MgO}$ .
  - Mixed crystals with  $\text{CaO}$  ( $\text{Mg}_x\text{Ca}_{1-x}\text{O}$ ) should allow elimination of intrinsic birefringence problem in this material.
- These approaches require some materials research to qualify/improve materials. But the smaller (thinner) the optic, the easier to implement. Can the industry find design solutions to utilize these high index materials with small path lengths?